

# (12) UK Patent Application (19) GB (11) 2 299 345 (13) A

(43) Date of A Publication 02.10.1996

(21) Application No 9605507.4

(22) Date of Filing 15.03.1996

(30) Priority Data

(31) 95006706

(32) 28.03.1995

(33) KR

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(51) INT CL<sup>6</sup>

C23C 16/56 16/34

(52) UK CL (Edition O )

C7F FHE FR916 F802 F809

U1S S1421 S2061

(56) Documents Cited

EP 0630990 A2

EP 0446988 A1

(58) Field of Search

UK CL (Edition O ) C7F FACE FACX FAHE FAHX FAXE

FAXX FHB FHE FHX , H1K KHAAB KJACN

INT CL<sup>6</sup> C23C 14/06 14/58 16/34 16/56 18/12 , H01L  
21/285

Online: WPI, CLAIMS

(54) A method of making, and a device including, a titanium nitride layer

(57) A method for making a titanium nitride (TiN) layer, includes the steps of forming the TiN layer from a source material, and exposing the TiN layer using hydrogen optionally together with nitrogen plasma gases. The effect is produced that the resistivity of the TiN layer increases by minimising the impurities therein and by decreasing the porosity thereof, such that the electrical stability of the TiN layer is increased.

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A METHOD OF MAKING, AND A DEVICE INCLUDING, A  
TITANIUM NITRIDE LAYER

The present invention relates to a method of making a titanium Nitride (TiN) layer, which is commonly used as a glue layer for tungsten and a diffusion barrier layer in aluminum (Al) metallization processes, and a device  
5 employing the layer. The method to be described below is particularly suitable for removing carbon and oxygen atoms which exist in the TiN layer.

Generally, in semiconductor manufacturing processes, a TiN layer has been widely used as a diffusion barrier  
10 layer and as a glue layer. Two methods for forming a TiN layer are known. One of these methods is a physical vapour deposition method (hereinafter, referred to as the PVD method) and the other method is a chemical vapour deposition method (hereinafter, referred to as the CVD  
15 method). The CVD method has been generally used for forming the TiN layer because of the excellent step-coverage.

The TiN layer is made by pyrolyzing source materials such as tetrakisdiethlyaminotitanum (TDMAT) and  
20 tetrakisdiethlyaminotitanum (TDEAT), and the TiN layer is porous.

However, since a TiN layer which is made by pyrolyzing includes carbide and oxide, it has a high resistivity of about  $10^4 \mu\text{ohm-cm}$  or more. Also, when the  
25 TiN layer is exposed to air, the TiN layer absorbs moisture and oxygen due to its porosity. In the case in

which the TiN layer is exposed for about twenty-four hours, the resistivity of the exposed TiN layer may be three and a half times as high as that of a TiN layer which has not been so exposed. Consequently, the quality of the TiN layer deteriorates.

A feature of a method for decreasing the resistivity of a TiN layer which is exposed to the air, to be described below as an example, is that it minimises the impurities therein using plasma gases.

In a particular arrangement to be described below as an example, a method of making a titanium nitride (TiN) layer, includes the step of forming the TiN layer out of a source materials, and exposing the TiN layer using hydrogen and nitrogen plasma gases.

In another arrangement to be described below as an example, a method of making a titanium nitride (TiN) layer, includes the step of forming the TiN layer out of source materials, and exposing the TiN layer using the hydrogen plasma gas.

An embodiment illustrative of the present invention will now be described by way of example.

First, a TiN Layer is formed using the CVD method by pyrolyzing TDMAT or TDEAT. Next, a primary plasma treatment is applied to the TiN layer using nitrogen and hydrogen gases. That is to say, the TiN layer is exposed to the nitrogen and the hydrogen gases.

In one preferred embodiment, the primary conditions are as follows:

- 1) the amount of the nitrogen gas: 100-500 sccm
- 2) the amount of the hydrogen gas: 100-500 sccm
- 5 3) the temperature: 200-500°C
- 4) the pressure: 0.5-5Torr
- 5) the RF power: 200-700W
- 6) the processing time: 10-60seconds

10        At this time, the primary plasma treatment is performed without any delay time in the chamber where the TiN layer is formed, or in another chamber attendant on the exposure of the TiN layer to the air.

      After first treating the TiN layer, a secondary  
15 plasma treatment is performed using the nitrogen gas.

      In one preferred embodiment, the secondary treatment conditions are as follows:

- 1) the amount of the nitrogen gas: 100-500sccm
- 2) the temperature: 200-500°C
- 20 3) the pressure: 0.5-5Torr
- 4) the RF power: 200-700W
- 5) the processing time: 10-60 seconds

      The active hydrogen ions in the primary plasma  
25 treatment penetrate into the TiN layer, and dissociate the bonds of  $-C=N=C=N-$  and  $=C=O$  radicals which exist in the TiN layer, thereby forming the chemical combination with the dissociated carbon and oxygen atoms. On the other hand, the by-products formed by this chemical

combination consist of  $\text{CH}_4$  and  $\text{H}_2\text{O}$  which are released.

Furthermore, the active nitrogen ions prevent the  
 5 oxygen ions, which exist in the processing chamber, from  
 being absorbed in the TiN layer, and occupy the vacancies  
 which are formed by the release of the  $\text{CH}_4$  and the  $\text{H}_2\text{O}$ .

Next, the secondary plasma treatment is applied to  
 the TiN layer to which the primary plasma has been  
 10 applied, such that the amount of nitrogen in the TiN  
 layer is maximised.

As a result, a number of combinations between  
 titanium and nitrogen can be achieved by the plasma  
 treatments. Accordingly, the density of the TiN layer to  
 15 which the plasma treatments are applied is denser than  
 that of the TiN layer to which the treatments are not  
 applied, and a TiN layer having a lower resistivity can  
 be achieved.

Table <1> shows the variation in the resistivity of  
 20 the TiN layer against exposure times in air in cases in  
 which the TiN layer is formed.

TABLE<1> resistivity of the TiN layer

exposure time to the air	resistivity	( $\mu$ ohm-cm)
	plasma treatment	no plasma treatment
0 hour	19706	2714
22 hours	70044	3922
47 hours	93376	4249
73 hours	112009	4444

\*1st plasma treatment :

- 1) temperature : 450°C
- 2) pressure : 2 Torr
- 3) RF power : 350W
- 4) hydrogen : 200sccm
- 5) nitrogen : 300sccm
- 6) time : 30seconds

\*2nd plasma treatment :

- 1) temperature : 450°C
- 2) pressure : 2 Torr
- 3) RF power : 350W
- 4) nitrogen : 300sccm
- 5) time : 30seconds

Also, with reference to table <1>, the secondary treatment conditions are the same as for the primary treatment conditions, except that only a nitride plasma gas in an amount of 300sccm is used.

As shown in table <1> above, the resistivity of the TiN layer decreases considerably.

Furthermore, table <2> below shows the difference in stress and table <3> below shows the reduction of oxygen and carbon atoms in the TiN layer without and with a plasma treatment respectively.

TABLE<2> stress of the TiN layer

	no plasma treatment		plasma treatment	
delay time	0 hour	24 hours	0 hour	24 hours
stress(dyne/cm <sup>2</sup> )	-9.00E+08	-1.30E+09	-6.70E+09	-7.70E+09
stress(%)	44 %		15 %	

TABLE<3> composition of the TiN layer

	no plasma treatment (at %)	plasma treatment (at %)
Ti	37	45
C	29	18
N	21	27
O	13	10

Another embodiment illustrative of the present invention will now be described by way of example.

5 In this embodiment, the primary plasma treatment involves the application of only one of the nitrogen and hydrogen gases to the TiN layer which is formed by pyrolyzing TDMAT or TDEAT. At this time, all the treatment conditions are the same as those of the previously  
10 described embodiments.

Of course, only one of the two step treatments can be used according to characteristics of the TiN layer.

As stated above, the present invention has the effect that the resistivity of the Tin layer increases by  
15 minimising the impurities therein and by decreasing the porosity thereof. Accordingly, use of the present invention can increase the electrical stability of a TiN layer.

It will be understood that the invention is  
20 concerned primarily with the production of semiconductor and other devices, although its application is not limited thereto, and that the scope of the protection sought extends to devices employing a titanium nitride layer made by a method within the scope of the  
25 accompanying claims.

Although preferred embodiments of the invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions as well as other embodiments

are possible, without departing from the scope of the invention as defined in the accompanying claims.

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CLAIMS

1. A method of making a titanium nitride (TiN) layer,  
5 including the steps of forming a TiN layer from a source material, and exposing the TiN layer to hydrogen and nitrogen plasma gases.
2. A method as claimed in claim 1, wherein the step of  
10 exposing the TiN layer is carried out in a chamber at a temperature within the range of 200-500°C, and at a pressure within the range of 0.5-5Torr, and employing radio frequency power within the range of 200-700W.
- 15 3. A method as claimed in either claim 1 or claim 2, wherein the amount of the hydrogen and nitrogen plasma gases is each between 100-500sccm.
- 20 4. A method as claimed in any one of the preceding claims wherein the step of exposing the TiN layer is carried out for 10-60 seconds.
5. A method as claimed in claim 1, wherein the step of exposing the TiN layer further includes the step of  
25 re-exposing the TiN layer to nitrogen plasma gas.
6. A method as claimed in claim 5, wherein the step of re-exposing the TiN to the nitrogen plasma gas is carried out in a chamber at a temperature within the range of

200-500°C, a pressure within the range of 0.5-5Torr, and  
employing radio frequency power within the range of 200-  
5 700W.

7. A method as claimed in claim 5, wherein the amount  
of the nitrogen plasma gas in the re-exposing step is  
100-500sccm.

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8. A method as claimed in claim 5, wherein the step of  
re-exposing the TiN layer is carried out for 10-60  
seconds.

15 9. A method of making a titanium nitride (TiN) layer,  
including the steps of forming a TiN layer from a source  
material, and exposing the TiN layer using a hydrogen  
plasma gas.

20 10. A method as claimed in claim 9, wherein the step of  
exposing the TiN layer is carried out in a chamber at a  
temperature within the range of 200-500°C, and at a  
pressure within the range of 0.5-5Torr, and employing  
radio frequency power in a range of 200-700W.

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11. A method as claimed in claim 10, wherein the amount  
of the hydrogen plasma gas is between 100-500sccm.

12. A method as claimed in claim 10, wherein the step of

exposing the TiN layer is carried out for between 10-60 seconds.

- 5 13. A method as claimed in claim 9, wherein the step of exposing the TiN layer further includes the step of re-exposing the TiN layer to nitrogen plasma gas.

- 10 14. A method as claimed in claim 13, wherein the step of re-exposing the TiN to the nitrogen plasma gas is carried out in a chamber at a temperature within the range of 200-500°C, at a pressure within the range of 0.5-5Torr, and employing radio frequency power in the range of 200-700W.

- 15 15. A method as claimed in claim 13, wherein the amount of the nitrogen plasma gas employed in the re-exposing step is between 100-500sccm.

- 20 16. A method as claimed in claim 13, wherein the step of re-exposing the TiN layer is carried out for between 10-60 seconds.

- 25 17. A method as claimed in claim 1 including the steps described herein with reference to either of the two embodiments described herein.

18. A device including a titanium nitride layer made by a method as claimed in any one of the preceding claims.



# The Patent Office

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Application No: GB 9605507.4  
Claims searched: 1-8,17, in part18

Examiner: Peter Beddoe  
Date of search: 18 April 1996

## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK CI (Ed.O): C7F (FHB,FHE,FHX,FACE,FACX,FAHE,FAHX,FAXE,FAXX); HIK  
(KHAAB,KJACN)  
Int CI (Ed.6): C23C (14/06,14/58,16/34,16/56,18/12); H01L 21/285  
Other: Online: WPI, CLAIMS

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A,Y	EP 0630990 A2 (APPLIED) see esp col. 5 l. 5-42; col. 7 l. 6-19	Y=1
Y	EP 0446988 A1 (EINIRICERCHE) see esp Ex 1	Y=1

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| X Document indicating lack of novelty or inventive step   | A Document indicating technological background and/or state of the art.  |
| Y Document indicating lack of inventive step if combined with one or more other documents of same category. | P Document published on or after the declared priority date but before the filing date of this invention.          |
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